Influence of quantum confinement on the ferromagnetism of (Ga,Mn)As diluted magnetic semiconductor

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We investigate the effect of quantum confinement on the ferromagnetism of diluted magnetic semiconductor $Ga_{1-x}Mn_xAs$ using a combination of tight-binding and density functional methods. We observe strong majority-spin Mn *d*-As *p* hybridization, as well as half metallic behavior, down to sizes as small as 20 Å in diameter. Below this critical size, the doped holes are self-trapped by the Mn-sites, signalling both valence and electronic transitions. Our results imply that magnetically doped III-V nanoparticles will provide a medium for manipulating the electronic structure of dilute magnetic semiconductors while conserving the ferromagnetic properties and even enhancing it in certain size regime.

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Over the last few years there has been an explosively rapid increase of activity in two frontier areas of semiconductor research: diluted magnetic semiconductors (DMSs) and semiconductor quantum dots. The renewed interest in diluted magnetic semiconductors [1,2] was motivated by the discovery of ferromagnetism in $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$ [3,4]. Such ferromagnetic semiconductors are enabling materials for the emerging technology of *spintronics* [5]. Here, in addition to the charge degree of freedom of conventional electronics, the spin degree of freedom can also be used so that signals can be stored and processed simultaneously on the same device component [1]. In addition, DMSs have been used to inject spin into normal semiconductors [6,7], where enormous spin life-time and coherence [8] have been demonstrated. These are two key ingredients for the physical realization of solid state quantum computing based on the spin degree of freedom [9].

The second frontier area, the study of semiconductor quantum dots, exploits the fact that by reducing the size of a semiconducting material, typically below the Bohr exciton radius, it is possible to tune its electronic and optical properties [10]. The changes result from the confinement of the electron and hole wavefunctions by the potential of the finite sized semiconductor nanoparticle, thereby increasing their energies as the particle size is decreased. This *quantum size effect* can have spectacular and desirable effects on the material properties that have already been utilized for various device purposes. The most obvious applications are in tailoring of the band gap for specific applications, such as the tuning of the absorption or emission energy in electronic, electro-optical, opto-electronic or purely optical devices.

In this paper we explore the integration of the fields of diluted magnetic semiconductors and semiconductor quantum dots in a theoretical study of nanoparticles made from the DMS material, (Ga,Mn)As. Various experimental groups are actively pursuing the synthesis of magnetic semiconducting nanoparticles, and the production of magnetically-doped II-VIs, including CdS [11], ZnS [12], CdSe [13] and ZnSe [14], has already been achieved. The chemistry of III-V nanocrystal growth makes the synthesis of (Ga,Mn)As nanoparticles more challenging, therefore a preliminary theoretical investigation is sensible before launching a large synthetic effort. The main question that we answer in this work is whether the conditions that lead to ferromagnetism in bulk (Ga,Mn)As - namely the combination of strong Mn *d*-As *p* hybridization in the majority spin band, and a half-metallic band structure allowing hole-doping of the majority spin channel - persist as the size of the system is reduced. Our results clearly establish that quantum confinement does not have a detrimental effect on the magnetic properties of (Ga,Mn)As nanoparticles down to very small sizes. As a consequence it is possible to exploit the quantum confinement effect to tune the electronic properties of (Ga,Mn)As nanocrystals over a very wide size range while retaining the desirable ferromagnetism or even enhancing it. Additionally, we see drastic changes in the electronic and magnetic properties at very small (< 20 Å diameter) sizes, arising from competition between different subparts of the electronic degrees of freedom. These changes eventually lead to the destruction of the essential electronic structural features required for ferromagnetism in ultra-small nanoparticles.

There is in fact no *a-priori* reason that the magnetic properties of magnetically doped semiconductor nanoparticles should be the same as those of the corresponding bulk system. Bulk (Ga,Mn)As is a half metallic ferromagnet [15] (HMFM) with 100% spin polarization of the states at the Fermi energy, E_F. Half-metallic ferromagnetism requires a very specific arrangement of the various bands (in this case majority and minority spin Mn 3*d* with respect to the Ga and As *s*, *p* states) such that a gap opens for one spin channel only. However the energy levels of these states shift in nanoparticles due to the quantum size effect, and the extent of the shift

depends on both the size of the nanoparticle and the effective masses of the electrons and holes. In particular, the transition metal $3d$ bands in a doped semiconductor are rather flat compared to the s and p valence and conduction bands of the host. This results in a rapid shift in the s and p derived bands and a relative insensitivity of the d band energy position as the nanoparticle size is reduced. Thus the underlying electronic structure of the doped nanoparticle will change rapidly and may become incompatible with the HMFM state. Such a loss of half-metallicity would in turn destabilize the ferromagnetism, limiting the tunability of the electronic properties with size if the magnetic properties need to be retained intact.

We calculate the electronic structure of Mn-doped GaAs nanoparticles as a function of size using a second nearest neighbor tight-binding (TB) method [16]. We obtain the TB parameters by fitting to our density functional band structure calculations of the corresponding bulk systems. Our numerical DFT implementation uses a pseudoatomic orbital basis set and pseudopotentials, within the local spin density approximation (LSDA). Details of the method and its optimization can be found in reference [15]. The first step in the TB parameterization is to fix the Ga and As on-site energies and the Ga-Ga, As-As and Ga-As hopping integrals, by fitting to the GaAs band structure along several directions in k-space. In this fit we use 35 k-points and we consider all the eigenvalues up to the conduction band. Then we repeat the fitting procedure for both the spin bands of MnAs. In this case we do not change the As-As hopping integrals and we allow the As on-site energies to be only rigidly shifted with respect to their values in GaAs. We do not allow spin-splitting of the Mn s and Mn p orbitals, since only the d orbitals are magnetically active. Finally we fix the remaining Ga-Mn parameters by fitting to the calculated band structure of a monolayer GaAs/MnAs superlattice.

$Ga_{1-x}Mn_xAs$ nanoparticles are generated by starting with a central Ga atom surrounded by four As atoms, then progressively adding successive shells of Ga and As atoms in the bulk GaAs zincblende structure. Mn atoms are randomly substituted at the Ga sites keeping the composition close to $x = 0.05$ in every case. The surface states of the clusters are passivated to quench the dangling bonds. We have investigated particles ranging in size from 6.0 Å diameter (containing 17 atoms) to 71.0 Å diameter (9527 atoms). We use exact diagonalization of the TB Hamiltonian for the small clusters (up to 25.0 Å containing 525 atoms) and the Lanczos method for larger clusters.

In Fig. 1a, we show our calculated DFT majority and minority spin densities of states (DOSs) of bulk $Ga_{1-x}Mn_xAs$ with $x = 0.0625$, along with the partial Ga s, p, As p and Mn d DOS. As previously reported [15], the material is a half metallic ferromagnet, with a gap in the minority spin DOS at E_F, but no gap in the majority channel [17]. The metallic majority spin DOS at E_F is comprised largely of As p states, suggesting that hole doping at the top of the valence band by the Mn^{2+} $3d^5$ ions, and subsequent polarization of the mobile charge carriers by interaction with the exchange-split energy levels of Mn d^5 [18], is responsible for the HMFM state. The orbital resolved DOS for the Mn $3d$ states is qualitatively different for majority and minority spins. The majority channel has extensively mixed states over the -1 to -4 eV energy range due to the strong hybridization between the Mn $3d$ and the As p states. In contrast, the DOS of the Mn $3d$ states for the minority spin shows a sharp feature at ∼1.5 eV above E_F with minimal admixture from other states. This difference is due to the fact that in the majority spin the Mn $3d$ states are in the middle of the valence band of GaAs, thereby mixing extensively with the As p. In contrast, the minority spin Mn $3d$ states fall in the GaAs gap, thereby remaining relatively unmixed. The DOS for the extended solid obtained from the tight binding Hamiltonian is shown in Fig. 1b. All the features of the DOS, including the HMFM behavior, are reproduced extremely well by the TB calculation, confirming the accuracy of our parameterization.

In the limit of large size, the electronic properties of semiconductor nanoparticles must approach asymptotically those of the corresponding bulk semiconductor. The calculated DOS for a 71.0 Å diameter cluster, shown in Fig. 1c, is indeed similar to that of the infinite solid. Clearly smaller particles are required to see any strong effect of quantum confinement. Our calculations of the electronic structures of progressively smaller-sized nanoparticles (not shown here) indicate that qualitatively similar electronic properties persist down to a very small size (∼25 Å diameter) although the band gap increases monotonically with decreasing size as expected. In Fig. 2a we show the calculated majority and minority spin DOS for a 25.0 Å diameter nanoparticle. We see that even such a small particle is both half-metallic and has strong Mn $3d$ - As p hybridization, therefore has all the indications for being ferromagnetic. This is remarkable, since it implies that it is possible to exploit the tunability of nanoparticles to tailor-make materials with specific electronic properties, without sacrificing the ferromagnetism. For example, the gap (1.4 eV) in the down-spin channel in this cluster is substantially larger than that in the larger 71.0 Å diameter particle (0.55 eV), or in the bulk (0.4 eV). So, for example, such nanoparticles could be used as a source of polarized light over a broad range of wavelengths.

However the 25.0 Å diameter (Ga,Mn)As nanoparticle is close to the size limit below which the essential properties of the bulk magnetic semiconductor are no longer retained. At smaller sizes, we see remarkably rapid changes in the electronic structures with decreasing size, signalling a complete change of electronic and magnetic properties. In fact we observe a cross-over behavior, akin

to a valence as well as a metal-insulator transition, that is driven by the quantum size effect. We illustrate this in Fig. 2 where we also plot our calculated DOSs of 18.5 and 12.1 Å diameter nanoparticles. Compared to the 25.0 Å nanoparticle, the DOS of the 18.5 Å particle (Fig. 2b) shows a substantial increase of the energy gap in the down-spin channel, as a consequence of the enhanced confinement, and a significant reorganization of the orbital contributions to the DOS near E_F, particularly in the majority channel. We find that the states close to E_F develop a significant amount of Mn d character, whereas the larger particles (Fig. 1c) and the infinite solid (Figs. 1a and 1b) have almost negligible contribution from the Mn d states at E_F. Simultaneously, the Mn d states in the majority channel are reduced in bandwidth compared to the larger clusters. For example the majority spin Mn d band width in 12.1 Å diameter nanoparticles (shown in Fig. 2d) is ∼1 eV narrower than that in the bulk solid. These results are easily understood in terms of quantum confinement effects: the GaAs s and p states, with low effective masses, shift very rapidly compared to the higher effective mass Mn d states. As the GaAs valence and conduction bands shift away from each other, majority spin Mn d states begin to appear at the top of the valence band. There is a decrease of the As p band width upon size reduction which is also primarily responsible for the reduced bandwidth of the Mn d band in the majority channel, through the strong hybridization between the Mn d and the As p orbitals. In contrast, the Mn d minority spin states continue to form a narrow peaked structure a couple of eVs above the Fermi energy even for the smallest nanoparticles.

There are interesting consequences of these movements of the energy levels, *via* changes in the Mn d characters in the highest occupied molecular orbital (HOMO) with the size of the clusters (Fig. 3). The percentage Mn d character at E_F is ∼8% in the extended solid as well as in the large clusters, indicated by the horizontal dotted line in Fig. 3. The Mn d character begins to increase appreciably below about 35 Å due to the downward shift of the valence band. This approach of the Fermi energy towards the Mn d majority state will in fact enhance the effective exchange coupling between the localized Mn d^5 spins and the conduction band [18] and thereby enhance the T_c with decreasing cluster size. However, as the shift of the top of the valence band continues beyond the Mn d majority state, the holes that were originally doped at the top of the valence band are increasingly trapped by the Mn sites, driving a Mn valence transition. This is signalled by the sharp rise in the Mn character in HOMO (Fig. 3) below ∼20 Å cluster size with as much as 92% Mn d contribution for the 6 Å clusters. This is also clearly shown by the change in the average Mn d occupancy, $< n_d >$. It should be noticed that this quantity cannot be used to determine directly a formal oxidation state of the Mn sites, due to the presence of substantial covalent admixture of Mn states with the GaAs states. We calculate that $< n_d >$ is about 5.23 in the 25.0 Å nanoparticle, corresponding to the formally divalent Mn^{2+} state. However, $< n_d >$ changes very rapidly with decreasing size below 25.0 Å to become 4.37 for the smallest sized 6.0 Å cluster. This change of almost unity in $< n_d >$ between 25.0 Å and 6.0 Å clusters indicates a valence transition with the Mn^{2+} ions self-trapping the doped holes, resulting in Mn^{3+} and the removal of the doped holes from the top of the valence band of GaAs. This, along with the absence of any substantial kinetic stabilzation *via* the strong antiferromagnetic exchange splitting of the conduction states [18] due to the placement of the valence band below the Mn majority spin state, will occur in particles smaller than ∼20 Å diameter, leading to an insulating state which is unable to sustain ferromagnetism.

In conclusion we have studied the effect of quantum size confinement on the magnetic properties of (Ga,Mn)As nanoparticles, using an LSDA-derived TB parameterization. We find that the nanoparticles retain the desirable ferromagnetic properties observed in bulk (Ga,Mn)As down to diameters as small as ∼20 Å even enhancing the magnetism over a certain size regime. For particles larger than this critical size, we find an half-metallic density of states, with a polarized As p hole at the Fermi energy. Smaller clusters show a large contribution of the Mn d state at E_F, eventually leading to the disappearance of the magnetic state. These results suggest that the electronic properties (in particular the band gap and also possibly T_c) of diluted magnetic semiconductor nanoparticles can be manipulated by controlling the cluster size very effectively.

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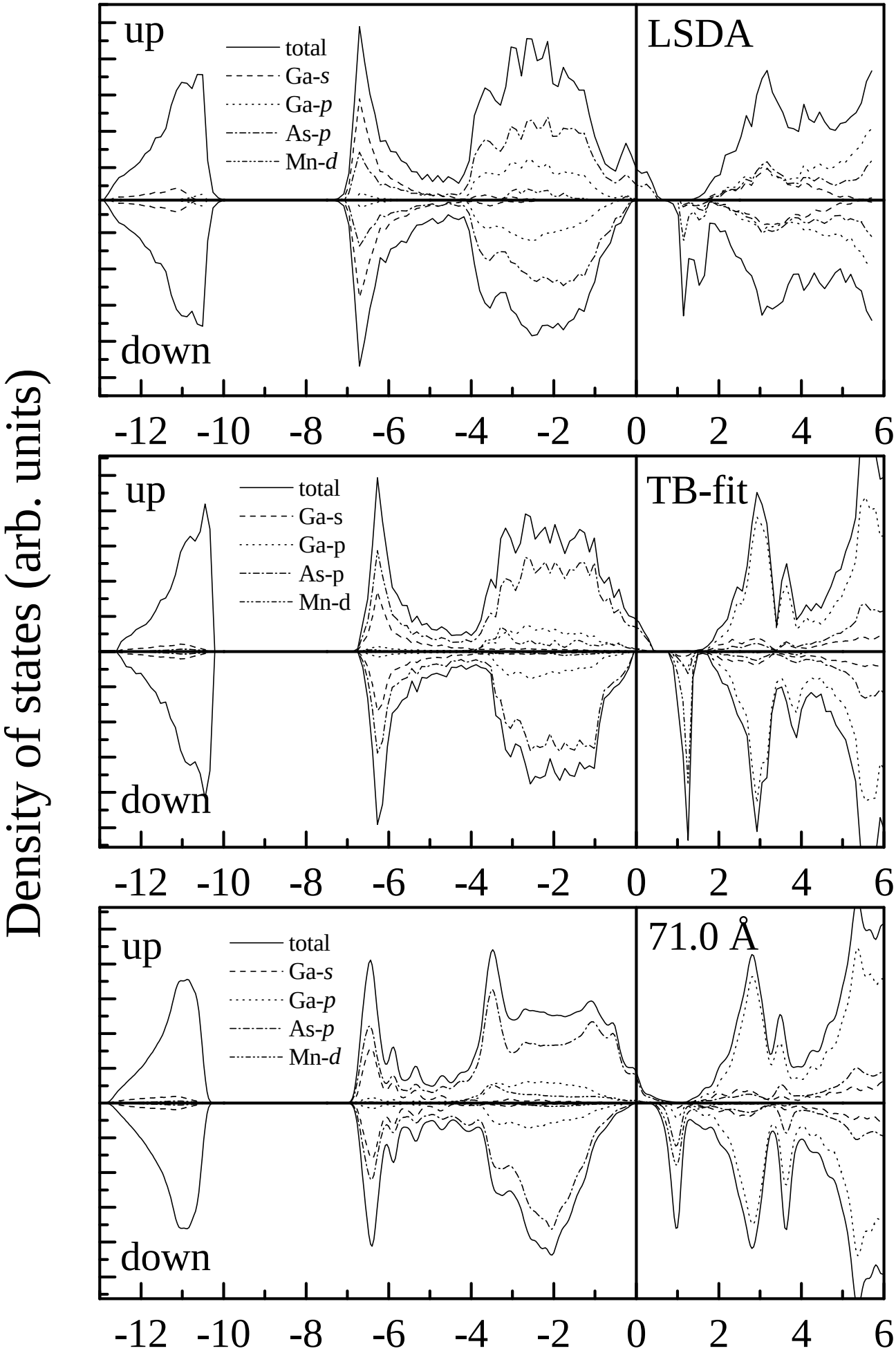
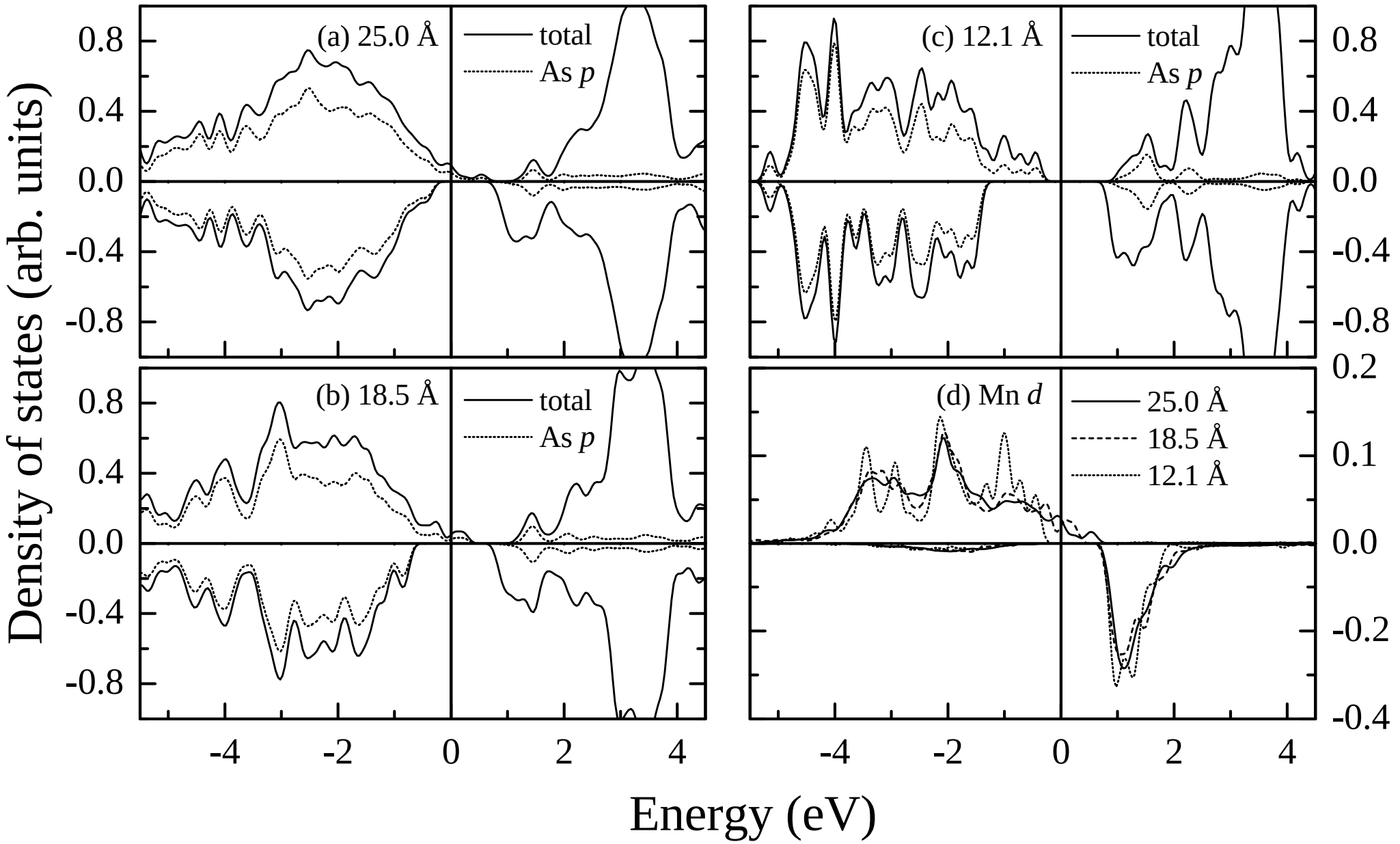
FIG. 1. Density of states for $Ga_{1-x}Mn_xAs$ with $x = 0.0625$ calculated with different methods: (a) LSDA calculation for the bulk, (b) tight-binding calculation for the bulk, (c) tight-binding calculation for a 71.0 Å cluster containing 9527 atoms (the cluster DOS has been broadened by a Gaussian with 0.3 eV FWHM).

FIG. 2. Density of states and partial As p density of states for three (Ga,Mn)As finite clusters: (a) 9 shells and 25.0 Å diameter, (b) 7 shells and 18.5 Å diameters, (c) 5 shells and 12.1 Å diameter, and (d) partial Mn d density of states for these three clusters. In all the panels the zero of energy corresponds to the E_F of bulk $Ga_{1-x}Mn_xAs$ with $x = 0.0625$. Note that the minority spin band gap increases with decreasing the size of the nanocrystal. The majority spin band gap collapses for the 12.1 Å nanocrystal. Also note that the DOS have been broadened by a Gaussian with 0.3 eV FWHM.

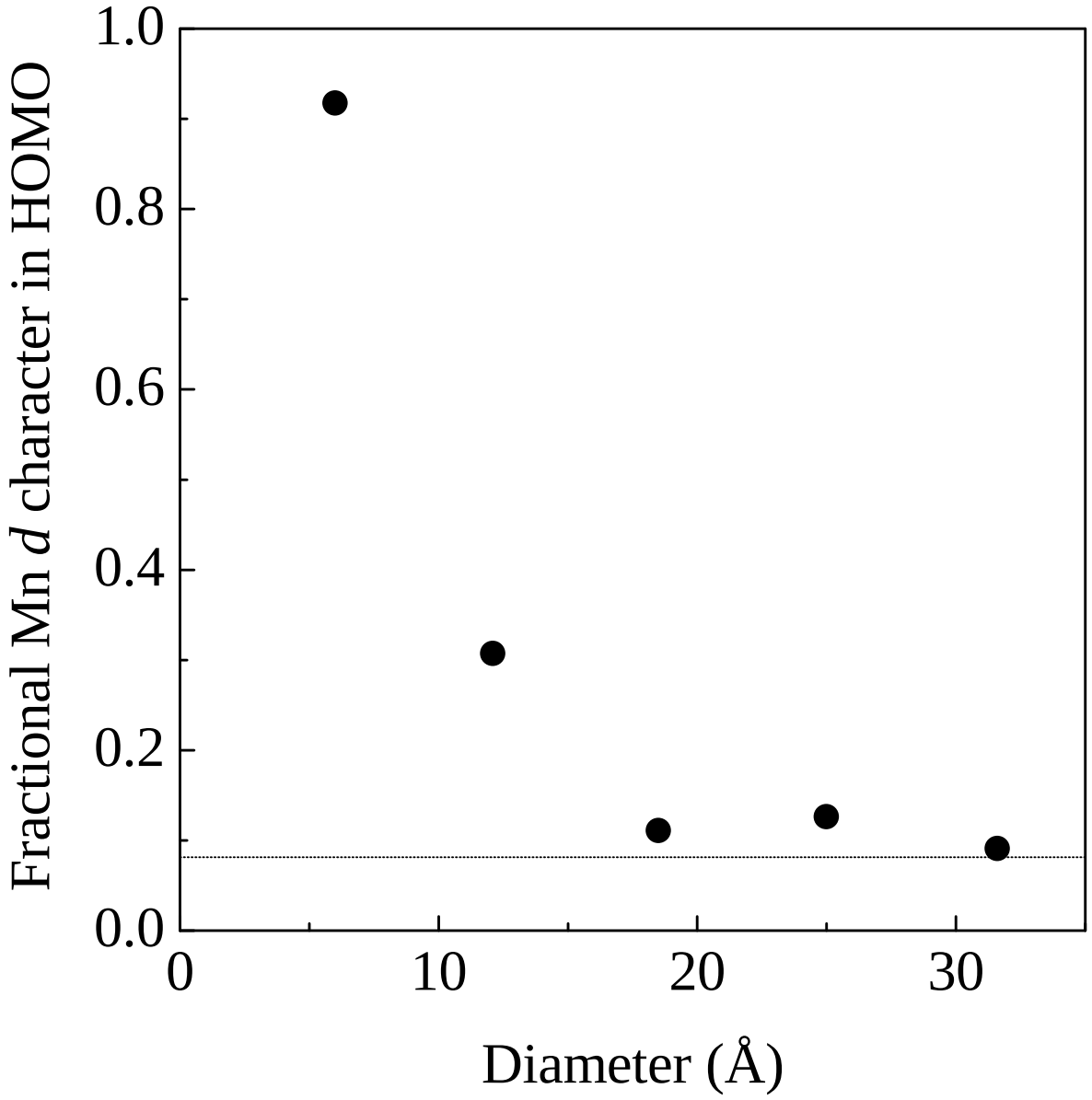
FIG. 3. (a) Mn d character of the HOMO as a function of the cluster size.



Sapra et al., Fig. 1



Sapra et al., Fig. 2



Sapra et al., Fig. 3